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(54) Method for the Pyrolytic Coating of Glass and Glass Ceramics

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ABSTRACT OF THE DISCLOSURE

Disclosed is a method for the pyrolytic preparation of transmission-reducing layers consisting of antimony oxide-doped tin oxide onto glass and glass ceramics, where the antimony oxide-doped tin oxide layer contains tin and antimony in a molar ratio of 1:0.2 to 1:0.5.

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METHOD FOR THE PYROLYTIC COATING OF GLASS AND GLASS CERAMICS

Field of the Invention

The invention relates to a method for the manufacture of pyrolytic layers on glass and glass ceramics resulting in a reduction of the optical transmission.

Background of the Invention

Glass that has an optical transmission in the visible range of less than 10% is used in many applications as glazing for protection against solar radiation, for example, in car glazing, particularly in glass sliding roofs (sun roofs or privacy glass).

Industrially, this requirement has been solved so far by the use of polymeric decorative films and/or ceramic silk screen prints which reduce the optical transmission by means of a pin diaphragm-type pattern (JP 88-272039). However, this method is not satisfactory from an industrial point of view, because the production process for laminated films is expensive and if films are glued to one side of a glass surface they separate over time resulting in a worsening of the appearance and also of the function.

It is standard knowledge of persons skilled in the art that glass tinted throughout its mass, which has an optical transmission of less than 10%, can only be manufactured at very high cost, and not using conventional methods, because the melt freezes.

Such glass types can be melted using very expensive industrial electromelting. This glass type is commercially available, but it can only be obtained in small quantities and at high prices, resulting from the cost of manufacture. Thus its use is considerably limited in cars.

Coatings with cobalt, chrome or iron acetylacetones are the state of the art (for example, DE-A-2052069, U.S. Patent No. 4,234,331). However, these layers do not reduce the optical transmission in the visible wavelength range to values of less than 20%. Glass which has been tinted throughout its mass using cobalt and chrome oxides also does not produce the desired reduction in transmission (for example, EP-A-0402685). In DE-A-3940660 values of 58% are mentioned for the optical transmission. In DE-A-2361744 a light transmission of 40% is indicated.

Sputter coatings processes also do not achieve a sufficient decrease in transmission (EP-A-0258635). In addition, the sputter coating process cannot be used on-line and it requires a considerably higher consumption of energy because the glass must subsequently be heated and introduced into an elevated vacuum.

Therefore, there is a need for a method which makes it possible to produce, in a simple manner, layers which absorb in the visible light wavelength range, as much as possible. Such a method is made available by the invention.

Brief Summary of the Invention

The present invention is a method for the manufacture of transmission-reducing layers onto glass (which term as used herein includes both glass and glass ceramics), where a layer consisting of antimony oxide-doped tin oxide, which contains tin and antimony in a molar ratio of 1:0.2 to 1:0.5, is applied pyrolytically onto the hot surface to be coated.

Detailed Description of the Invention

It is preferred to use, for the purpose of the present invention, a solution of tin and antimony compounds in an organic solvent and/or water, which solution is applied onto the hot surface to be coated, followed by the pyrolytic production of a layer made of oxides of these elements.

It is preferred, in this process, to apply the layer in a thickness of 50-1500 nm.

The glass surface that has thus been finished has a high optical absorption in the wavelength range between 0.300 μm and 0.700 μm. The optical transmission here is less than 10%. These industrial functional values of the antimony oxide-doped tin oxide layers so produced are thus substantially comparable to conventionally applied coatings.

The coatings obtained according to the invention are dark gray-violet in color on color-neutral float glass in daylight.

Because, in the case of the coating method according to the invention, technically proven application methods are used, defect-free layers are obtained.

The application methods are known from the coating of substrates with tin oxide. In that process, both a reduction of the electrical resistance of the surface so coated and an increase in infrared reflection are obtained. Industrially, these physical properties are used for heat-protective glazings or for surface heating of window panes, for example, car window panes, and refrigerated product display glazings.

To prepare such layers, suitable tin compounds (base compounds) are applied, preferably simultaneously with a doping agent, to the glass surface that has been heated to 400-800°C. The base tin compound forms a cohesive tin(IV) oxide layer on the surface of the glass or the glass ceramic. Fluorine, in particular, used as doping agent, increases the electrical conductivity and results in high infrared reflection. It is particularly easy to apply by spraying a suitable tin-containing solution for the application of the tin oxide layers onto the surfaces (see, for example, DE-A-3915232 and DE-A-3735574).

An additional known method for the pyrolytic coating of glass surfaces is the CVD process (chemical vapor deposition). In that process, the starting compounds in the vapor form are contacted with the glass surface (see, for example, DE-A-2361702).

Furthermore, it has become a proven technique to apply the starting compounds in the form of powders onto the substrate to be coated. Reference is made, as an example of the apparatus setup for industrial powder application, to EP-A-0095765.

Another object of the invention is a preparation for pyrolytic application of a transmission-reducing layer onto glass and glass ceramic, which contains:

(a) 97-70 parts by weight of one or more tin compounds, and

(B) 3-30 parts by weight of one or more antimony compounds and 0-60 wt%, with respect to a + b, of an organic solvent or solvent mixture and/or water.

Suitable tin and antimony compounds are, in particular, those that can be dissolved in water or organic solvents, or that can be vaporized without difficulty. Those compounds that are easy to transform into a fine-particle shape and that do not tend to form clumps are particularly suitable for powder application.

Examples of suitable tin-containing compounds are: tin tetrachloride, alkyltin trichloride (for example, monobutyltin chloride), dialkyltin dichloride (for example, dibutyltin dichloride), monoalkyltin oxide (for example, monobutyltin oxide), dialkyltin oxide (for example, dibutyltin oxide), monoalkyltin tricarboxylates (for example, monobutyltin triacetate), dialkyltin dicarboxylates (for example, dibutyltin diacetate), trialkyltin

carboxylate (for example, tributyltin acetate), dichlorotin dicarboxylates (for example, dichlorotin diacetate), aqueous, alcohol or ketone tin (IV) acid salts or mixtures of the above-mentioned tin-containing compounds. The alkyl groups and the carboxylates preferably contain 1 to 8 carbon atoms.

Examples of suitable antimony compounds are: antimony (III) chloride, antimony (V) chloride, antimony (III) oxide, antimony (IV) oxide, antimony (V) oxide, antimony (III) flouride, antimony (V) flouride, antimony oxychlorides, hexachloroantimonic acid, antimony alcoholates, and antimony acetylacetones. The alcoholates preferably contain 1 to 6 carbon atoms.

Possible organic solvents include alcohols (methanol, ethanol, isopropanol, butanol), ketones (acetone, methyl ethyl ketone, methyl isobutyl ketone), esters (acetic acid ethyl ester, acetic acid butyl ester) and/or water. As used herein, the term "organic solvent" includes individual compounds well as mixtures thereof.

In selecting the compounds, the intercompatibility of the components should be taken into account. The technical conditions employed, such as, for example, spraying apparatus or application using a vaporization apparatus, and the glass temperature or production rate, determine the type and concentration of the substances used in this coating formulation.

The preparation of the coating formulation is carried out in a simple manner by mixing in an

appropriate stirring vessel, where care must be taken that the coating formulation does not become excessively heated and, in the case of solutions, that no precipitation occurs. Ideally, the temperature should be kept clearly below the boiling point of the components.

The proportions of the components can, as indicated, vary within a broad range. However, the components must be present in a sufficient quantity in each case to meet the requirements of an industrial application, such as, for example, suitability for dosing and suitability for spraying.

The selection is based on the type and the composition of the substrate to be coated and on the industrial coating conditions.

Suitable solutions are, for example:

35.3% tin(IV) chloride
12.0% antimony(III) chloride
52.7% ethanol

43.25% butyltin trichloride
12.0% antimony(III) chloride
44.75% ethanol

60.0% butyltin trichloride
25.0% antimony(V) chloride
5.0% ethyl acetate
10.0% ethanol

54.5% dichlorotin diacetate
22.0% antimony(V) chloride

23.5% ethyl acetate
43.25% butyltin trichloride
12.0% antimony(III) chloride
44.75% ethanol

53.8% dibutyltin dichloride
15.9% antimony (III) chloride
30.3% butanol

80% butyltin trichloride
20% antimony (III) chloride

To carry out the coating method according to the invention, the preparation according to the invention is applied in the spray methods, CVD methods (chemical vapor deposition) or powder coating methods onto a surface which has first been heated. The temperature of the substrate should be 400-800°C, but the temperature should be less than the melting or softening temperature of the substrate in each case. In this process, a thin layer consisting of metal oxides of the metal components used develops on the hot surface as a result of oxidation and thermal decomposition. The solvent evaporates and/or decomposes.

A tin oxide/antimony oxide functional layer is thus produced on the surface as a result of pyrolysis. The thickness of this coating can be varied between 0.05 µm and 1.5 µm by dosing the quantities of the applied solution/mixture/powders. The molar ratio of tin to antimony determines the

reduction of the transmission for a given layer thickness. To achieve an optical transmission as low as possible, a molar ratio of 1:0.2 to 1:0.5, preferably 1:0.4 (tin:antimony) has been shown to be advantageous in the coating mixture.

The following examples are provided to further explain the invention.

Example 1

A solution was prepared which contained:
43.25% butyltin trichloride
8% antimony (III) chloride
48.75% ethanol

The solution was applied by spraying onto a flat glass disk (160 mm x 180 mm x 6 mm), which had first been heated for 5 min at an oven temperature of approximately 700°C, and which had been introduced by means of a pneumatic lift-off rotary installation into a spraying compartment with exhaust.

The glass plate which had been coated in this manner with a hand-held Walther spray gun (nozzle diameter 0.8 mm, spray pressure 1.5 b, spray distance approximately 35 cm, spray quantity 8 mL) presented the following values, with the above-mentioned spray quantities, after annealing, pressure reduction and cooling (Gardener Hazemeter HAZE-GARD Plus (according to ASTM D1003-61) and Beckman Instruments DU 60):

Optical transmission: 8.8%

Example 2

The procedure of Example 1 was repeated with a solution of:

34.3% butyltin trichloride
14% antimony (III) chloride
51.7% ethanol

The optical transmission (HAZE-GARD Plus) was determined to be 9.2%.

The disks which had been coated in this way could be annealed and bent without problem. Only if the bending radii were less than 1 m could very fine microcracks be observed for the first time under an optical microscope, however, industrially, bending radii on the order of magnituda of approximately 5 m are usually used.

Example 3

(CVD technique)

In a 250-mL four-neck flask the following solution was introduced which contained

24.1% antimony (III) chloride
75.9% butyltin trichloride.

Using gas-stream heating, dried compressed air was introduced through a neck into the flask and passed over the surface of the liquid. The temperature in the gas phase of the interior of the flask was approximately 140°C. The rate of

evaporation in the flask was approximately 71 g/h. Using another flask neck, the gas stream, which had been enriched with the vaporized components, was fed through a glass pipe onto the surface of a glass disk which had first been heated in a glazing furnace to 690°C.

A glass disk which had been coated in this manner had the following functional value:

Transmission (HAZE-GARD Plus): 9.2%

<u>Example 4</u>

(Direct application of powders)

Using a vibrating feed chute (model DR1000 from the Retsch Company) a mixture of

69 parts of monobutyltin oxide and

31 parts of antimony (III) chloride,

was applied onto a glass surface which had been heated to 650°C. A cohesive metal oxide film formed. This operation was then repeated an additional three times (heating time 5 min, powdering). After the annealing and pressure reduction, the disk so coated had the following functional value:

Transmission (HAZE-GARD Plus): 9.5%

CLAIMS

1. A method for the formation of a transmission-reducing layer on a glass surface, comprising heating said surface and applying to said heated surface a layer of a mixture of one or more antimony compounds and one or more tin compounds having a molar ratio of tin:antimony of 1:0.2 to 1:0.5, and pyrolyzing said mixture on said surface whereby a layer is formed consisting of antimony oxide-doped tin oxide.

2. A method according to Claim 1, wherein the layer is applied in a thickness of 50-1500 nm.

3. A method according to Claim 1 wherein the mixture applied to said surface is a solution of tin and antimony compounds in an organic solvent, water, or a mixture thereof.

4. A method according to Claim 2 wherein the mixture applied to said surface is a solution of tin and antimony compounds in an organic solvent, water, or a mixture thereof.

5. A composition useful in the pyrolytic formation of a transmission-reducing layer onto glass, which consists of:

a) 97-70 parts by weight of one or more tin compounds and

b) 3-30 parts by weight of one or more antimony compounds and

c) 0-60 wt%, with respect to a + b, of an organic solvent, water, or a mixture thereof.